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Crystal structure of 4-aminobenzoic acid–4-methylpyridine (1/1)

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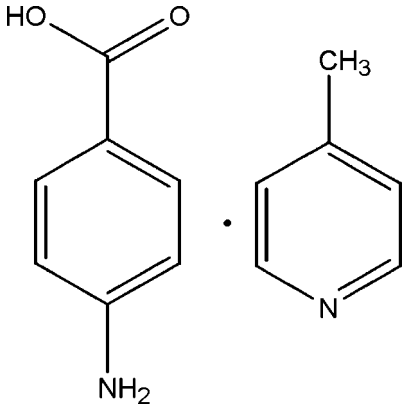
In the title 1:1 adduct, $C_6H_7N{\cdot}C_7H_7NO_2$, the carboxylic acid group is twisted at an angle of 4.32 (18)° with respect to the attached benzene ring. In the crystal, the carboxylic acid group is linked to the pyridine ring by an O—H···N hydrogen bond, forming a dimer. The dimers are linked by N—H···O hydrogen bonds, generating (010) sheets.

Keywords: crystal structure; adduct; O—H···N and N—H···O hydrogen bonds; layered structure.

CCDC reference: 1043592

1. Related literature

For background to pyridine derivatives, see: Tomaru *et al.* (1991). Katritzky *et al.* (1996); Akkurt *et al.* (2005). For related structures, see: Smith & Wermuth (2010); Hemamalini & Fun (2010); Kannan *et al.* (2012); Thanigaimani *et al.* (2012); Muralidharan *et al.* (2013).



2. Experimental

2.1. Crystal data

$C_6H_7N{\cdot}C_7H_7NO_2$
M_r = 230.26
Monoclinic, *Pc*
a = 7.5970 (7) Å
b = 11.6665 (12) Å
c = 7.6754 (8) Å
β = 114.200 (3)°
V = 620.49 (11) Å^3
Z = 2
Mo *Kα* radiation
μ = 0.09 mm^{-1}
T = 295 K
0.28 × 0.24 × 0.20 mm

2.2. Data collection

Bruker Kappa APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.977, T_{max} = 0.983
10064 measured reflections
2144 independent reflections
1458 reflections with $I > 2\sigma(I)$
R_{int} = 0.030

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.108
S = 1.03
2144 reflections
159 parameters
3 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.12 e Å^{-3}
$\Delta\rho_{min}$ = −0.13 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N2^{i}	0.84 (1)	1.81 (1)	2.644 (3)	177 (4)
N1—H1*A*···O2^{ii}	0.86	2.32	3.049 (3)	142
N1—H1*B*···O2^{iii}	0.86	2.17	3.031 (3)	174

Symmetry codes: (i) $x+1, y, z$; (ii) $x-1, y, z-1$; (iii) $x-1, -y, z-\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2015); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: HB7348).

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supporting information

Acta Cryst. (2015). E**71**, o125–o126 [doi:10.1107/S2056989015000791]

Crystal structure of 4-aminobenzoic acid–4-methylpyridine (1/1)

M. Krishna Kumar, P. Pandi, S. Sudhahar, G. Chakkaravarthi and R. Mohan Kumar

S1. Chemical context

Aminopyridine and its derivatives play an important role in heterocyclic chemistry (Katritzky *et al.*, 1996). Some pyridine derivatives possess nonlinear optical (NLO) properties (Tomaru *et al.*, 1991) and possess antibacterial and anti-fungal activities (Akkurt *et al.*, 2005). we herewith, report the synthesis and the crystal structure of (I) (Fig. 1).

S2. Structural commentary

The molecular structure of the title compound (I) is shown in (Fig. 1). It consists of two independent molecules in the assymetric unit. In the 4-aminobenzoic acid molecule, the carboxyl group is twisted at an angle of 4.32 (18)° with respect to the aromatic ring. In the 4-methylpyridine molecule, the pyridine ring (C8—C12/N2) is almost planar [maximum deviation 0.002 (3) Å]. The dihedral angle between the benzene ring (C1—C6) and pyridine ring (C8—C12/N2) is 57.11 (14)°.

S3. Supramolecular features

In the crystal structure, 4-aminobenzoate and 4-methylpyridine molecules are linked by weak intermolecular O—H···N hydrogen bonds and forms infinite one-dimensional chain along [0 0 1]. The adjacent 4-aminobenzoate molecules are connected by weak intermolecular N—H···O hydrogen bonds, forming $R^2_2(12)$ ring motif in a two-dimensional network in the (010) plane (Table 2 & Fig. 2).

S4. Database survey

Several similar structures containing methylpyridinium and nitrobenzoate molecules have been reported earlier: i.e., 2-Amino-5-methylpyridinium 2-aminobenzoate (Thanigaimani *et al.*, 2012); 2-Amino-5-chloropyridinium 4-amino-benzoate (Kannan *et al.*, 2012); 2-Amino-4-methylpyridinium 2-nitrobenzoate (Muralidharan *et al.*, 2013); 4-Methyl-pyridinium 2-carboxy-4,5-dichlorobenzoate monohydrate [Smith & Wermuth, (2010)]; 2-Amino-4-methylpyridinium 2-hydroxybenzoate [Hemamalini & Fun (2010)].

S5. Synthesis and crystallization

Equimolar quantity of 4-methylpyridine and 4-aminobenzoic acid were dissolved in methanol-water mixed solvent and colourless blocks of the title adduct were grown by slow evaporation of the solvents.

S6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The hydrogen atoms attached to C atoms and N atom were fixed geometrically and treated as riding with C—H = 0.93 Å (aromatic) or 0.96 Å (methyl) and N—H = 0.86 Å with Uiso(H) = 1.2 Ueq(C or N) or 1.5 Ueq(C) The hydroxyl H atom was located in a difference Fourier map, and refined with Uiso(H) = 1.2 Ueq(O) and distance restraint O—H = 0.82 Å.

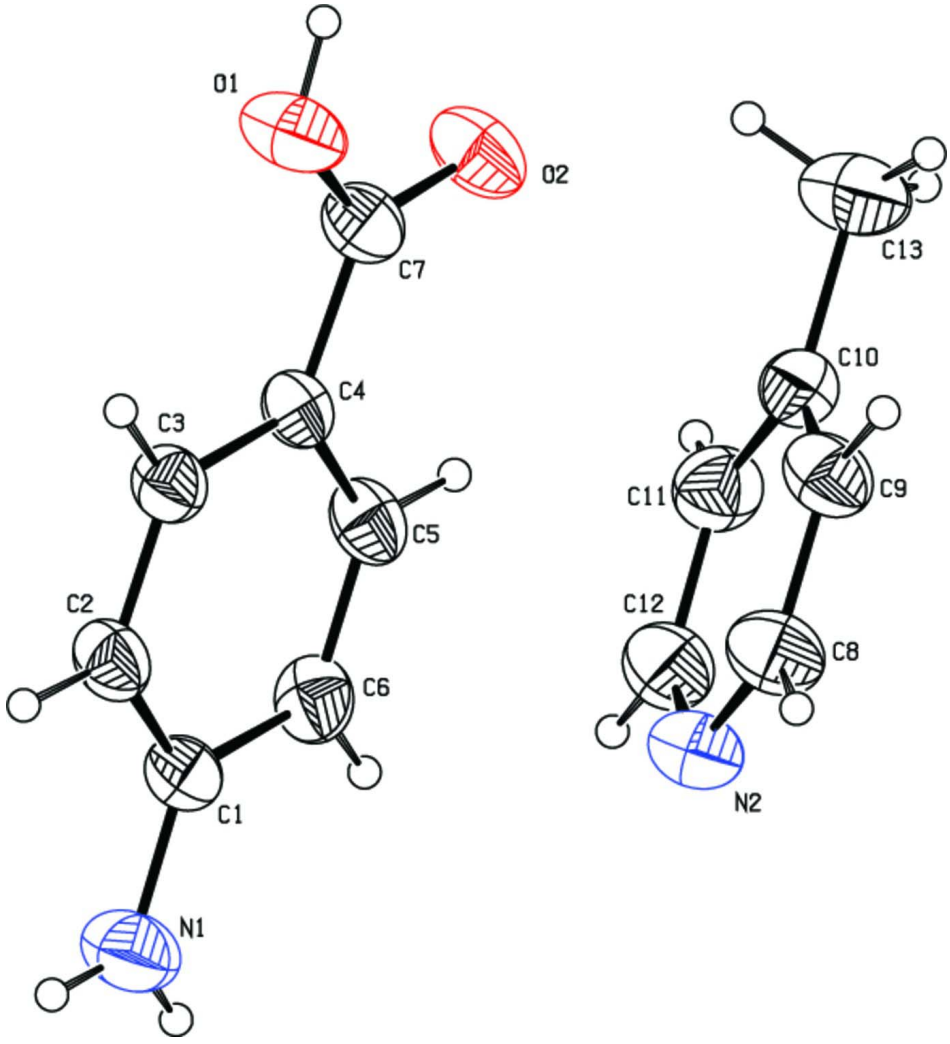

Figure 1

The molecular structure of (I), with 30% probability displacement ellipsoids for non-H atoms.

4-Aminobenzoic acid–4-methylpyridine (1/1)

Crystal data

$C_6H_7N·C_7H_7NO_2$
M_r = 230.26
Monoclinic, *Pc*
Hall symbol: P -2yc
a = 7.5970 (7) Å
b = 11.6665 (12) Å
c = 7.6754 (8) Å
β = 114.200 (3)°
V = 620.49 (11) Å^3
Z = 2
$F(000)$ = 244
D_x = 1.232 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2749 reflections
θ = 3.4–21.8°
μ = 0.09 mm^{-1}
T = 295 K
Block, colourless
0.28 × 0.24 × 0.20 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scan
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.977, T_{max} = 0.983
10064 measured reflections
2144 independent reflections
1458 reflections with $I > 2\sigma(I)$
R_{int} = 0.030
θ_{max} = 26.7°, θ_{min} = 3.4°
h = −9→8
k = −14→14
l = −9→9

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.108
S = 1.03
2144 reflections
159 parameters
3 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0554P)^2 + 0.0229P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.12 e Å^{-3}
$\Delta\rho_{min}$ = −0.13 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.013 (4)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2$sigma(F^2) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
C1	0.3693 (4)	0.1034 (2)	0.7149 (4)	0.0567 (6)
C2	0.4434 (4)	0.2029 (2)	0.6722 (4)	0.0591 (7)
H2	0.3671	0.2471	0.5675	0.071*
C3	0.6273 (4)	0.2362 (2)	0.7829 (3)	0.0558 (6)
H3	0.6737	0.3037	0.7529	0.067*
C4	0.7475 (4)	0.1730 (2)	0.9383 (4)	0.0508 (6)
C5	0.6737 (4)	0.0738 (2)	0.9798 (4)	0.0594 (7)
H5	0.7516	0.0294	1.0835	0.071*
C6	0.4892 (4)	0.0392 (2)	0.8724 (4)	0.0629 (7)
H6	0.4429	−0.0278	0.9043	0.076*
C7	0.9416 (4)	0.2104 (2)	1.0596 (4)	0.0587 (7)
C8	0.4371 (5)	0.4546 (2)	1.3188 (5)	0.0729 (8)
H8	0.3567	0.5148	1.3183	0.087*
C9	0.6306 (4)	0.4655 (2)	1.4263 (4)	0.0693 (8)
H9	0.6791	0.5319	1.4967	0.083*

C10	0.7534 (4)	0.3784 (2)	1.4304 (4)	0.0639 (7)
C11	0.6716 (4)	0.2836 (2)	1.3242 (4)	0.0718 (8)
H11	0.7487	0.2220	1.3229	0.086*
C12	0.4767 (5)	0.2790 (3)	1.2196 (4)	0.0766 (9)
H12	0.4249	0.2135	1.1479	0.092*
C13	0.9658 (5)	0.3866 (3)	1.5468 (6)	0.0954 (11)
H13A	1.0310	0.3941	1.4635	0.143*
H13B	1.0099	0.3186	1.6229	0.143*
H13C	0.9930	0.4524	1.6289	0.143*
N1	0.1840 (4)	0.0710 (2)	0.6087 (4)	0.0827 (8)
H1A	0.1113	0.1124	0.5137	0.099*
H1B	0.1395	0.0092	0.6364	0.099*
N2	0.3582 (3)	0.3627 (2)	1.2152 (4)	0.0722 (6)
O1	0.9921 (3)	0.30989 (17)	1.0123 (3)	0.0808 (6)
H1	1.109 (2)	0.324 (3)	1.076 (5)	0.121*
O2	1.0516 (3)	0.15755 (17)	1.1996 (3)	0.0778 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0545 (16)	0.0584 (15)	0.0526 (15)	−0.0071 (14)	0.0173 (13)	−0.0070 (14)
C2	0.0599 (17)	0.0581 (15)	0.0489 (15)	0.0009 (12)	0.0118 (13)	0.0088 (12)
C3	0.0582 (16)	0.0536 (13)	0.0509 (15)	−0.0050 (13)	0.0175 (13)	0.0058 (12)
C4	0.0529 (14)	0.0490 (12)	0.0442 (13)	0.0040 (12)	0.0135 (12)	0.0026 (12)
C5	0.0671 (18)	0.0516 (14)	0.0484 (16)	0.0021 (13)	0.0124 (14)	0.0046 (12)
C6	0.077 (2)	0.0518 (14)	0.0590 (17)	−0.0076 (14)	0.0273 (15)	0.0048 (13)
C7	0.0563 (17)	0.0532 (13)	0.0583 (17)	0.0045 (13)	0.0150 (14)	0.0003 (14)
C8	0.0630 (18)	0.0626 (16)	0.081 (2)	0.0031 (15)	0.0172 (16)	0.0007 (16)
C9	0.068 (2)	0.0617 (17)	0.0665 (19)	−0.0085 (14)	0.0150 (16)	−0.0042 (13)
C10	0.0579 (18)	0.0740 (17)	0.0585 (17)	−0.0045 (16)	0.0225 (14)	0.0063 (15)
C11	0.0680 (19)	0.0723 (18)	0.078 (2)	0.0015 (15)	0.0325 (18)	−0.0048 (16)
C12	0.077 (2)	0.0747 (19)	0.074 (2)	−0.0158 (17)	0.0260 (17)	−0.0171 (16)
C13	0.0604 (19)	0.105 (2)	0.104 (3)	−0.0070 (17)	0.0163 (18)	0.002 (2)
N1	0.0655 (16)	0.0852 (18)	0.0809 (18)	−0.0163 (13)	0.0132 (14)	0.0063 (15)
N2	0.0567 (14)	0.0719 (15)	0.0766 (16)	−0.0059 (13)	0.0157 (12)	−0.0023 (13)
O1	0.0588 (11)	0.0691 (12)	0.0883 (16)	−0.0105 (10)	0.0035 (11)	0.0130 (11)
O2	0.0678 (13)	0.0726 (12)	0.0665 (12)	0.0068 (10)	0.0006 (10)	0.0090 (10)

Geometric parameters (Å, º)

C1—N1	1.359 (4)	C8—H8	0.9300
C1—C2	1.387 (3)	C9—C10	1.371 (4)
C1—C6	1.397 (4)	C9—H9	0.9300
C2—C3	1.361 (4)	C10—C11	1.363 (4)
C2—H2	0.9300	C10—C13	1.493 (5)
C3—C4	1.380 (3)	C11—C12	1.366 (4)
C3—H3	0.9300	C11—H11	0.9300
C4—C5	1.379 (3)	C12—N2	1.319 (4)

C4—C7	1.452 (3)	C12—H12	0.9300
C5—C6	1.364 (4)	C13—H13A	0.9600
C5—H5	0.9300	C13—H13B	0.9600
C6—H6	0.9300	C13—H13C	0.9600
C7—O2	1.224 (3)	N1—H1A	0.8600
C7—O1	1.319 (3)	N1—H1B	0.8600
C8—N2	1.323 (3)	O1—H1	0.836 (10)
C8—C9	1.365 (4)		

N1—C1—C2	120.8 (2)	C8—C9—C10	119.9 (3)
N1—C1—C6	121.2 (2)	C8—C9—H9	120.0
C2—C1—C6	118.0 (2)	C10—C9—H9	120.0
C3—C2—C1	120.2 (2)	C11—C10—C9	116.6 (3)
C3—C2—H2	119.9	C11—C10—C13	121.7 (3)
C1—C2—H2	119.9	C9—C10—C13	121.7 (3)
C2—C3—C4	122.2 (2)	C10—C11—C12	120.2 (3)
C2—C3—H3	118.9	C10—C11—H11	119.9
C4—C3—H3	118.9	C12—C11—H11	119.9
C5—C4—C3	117.4 (2)	N2—C12—C11	123.4 (3)
C5—C4—C7	120.4 (2)	N2—C12—H12	118.3
C3—C4—C7	122.1 (2)	C11—C12—H12	118.3
C6—C5—C4	121.5 (2)	C10—C13—H13A	109.5
C6—C5—H5	119.2	C10—C13—H13B	109.5
C4—C5—H5	119.2	H13A—C13—H13B	109.5
C5—C6—C1	120.6 (2)	C10—C13—H13C	109.5
C5—C6—H6	119.7	H13A—C13—H13C	109.5
C1—C6—H6	119.7	H13B—C13—H13C	109.5
O2—C7—O1	120.9 (3)	C1—N1—H1A	120.0
O2—C7—C4	124.1 (2)	C1—N1—H1B	120.0
O1—C7—C4	115.0 (2)	H1A—N1—H1B	120.0
N2—C8—C9	123.3 (3)	C12—N2—C8	116.6 (3)
N2—C8—H8	118.4	C7—O1—H1	112 (3)
C9—C8—H8	118.4		

N1—C1—C2—C3	178.1 (3)	C3—C4—C7—O2	179.2 (3)
C6—C1—C2—C3	−0.5 (4)	C5—C4—C7—O1	−176.1 (2)
C1—C2—C3—C4	0.9 (4)	C3—C4—C7—O1	1.3 (3)
C2—C3—C4—C5	−0.5 (4)	N2—C8—C9—C10	0.0 (5)
C2—C3—C4—C7	−178.1 (2)	C8—C9—C10—C11	−0.2 (4)
C3—C4—C5—C6	−0.2 (4)	C8—C9—C10—C13	−179.7 (3)
C7—C4—C5—C6	177.4 (2)	C9—C10—C11—C12	0.4 (4)
C4—C5—C6—C1	0.5 (4)	C13—C10—C11—C12	179.9 (3)
N1—C1—C6—C5	−178.8 (3)	C10—C11—C12—N2	−0.4 (5)
C2—C1—C6—C5	−0.2 (4)	C11—C12—N2—C8	0.1 (5)
C5—C4—C7—O2	1.7 (4)	C9—C8—N2—C12	0.1 (5)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N2^{i}	0.84 (1)	1.81 (1)	2.644 (3)	177 (4)
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